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INHERENT BIAS  
IN NONLINEAR LEAST SQUARES ANALYSIS  
OF FIRST-ORDER KINETIC DATA

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## PREFACE

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# INHERENT BIAS IN NONLINEAR LEAST SQUARES ANALYSIS OF FIRST-ORDER KINETIC DATA

## 1. INTRODUCTION

It has become increasingly popular to use an unweighted nonlinear least squares analysis to evaluate first-order rate constants.<sup>1-3</sup> The typical procedure starts with a data set  $t_i, y_i$  and fits it to a function

$$p_t = a + b e^{-kt} \quad (1)$$

where  $p_i$  is the predicted (calculated) value of the measurement  $y_i$ . This is a relatively complex problem because the nonlinear fitting routine does not reduce algebraically (as does the linear version) so that various values of the constants  $a$ ,  $b$ , and  $k$  are tried, and a minimum variance is sought. It is used in preference to its linear analog

$$\ln(y_i - a) = -kt + \ln(b) \quad (2)$$

because the experimental uncertainties of the  $y_i$  values do not transform linearly into  $\ln$  space. The uncertainty of  $\ln(y_i - a)$  increases with time and in the unweighted procedure introduces a large potential error into the determination of  $k$ .

The shortcomings of the linear procedure are well known<sup>1,4-6</sup> but no one has carefully examined the difficulties inherent in the exponential fit routine. There is the tacit assumption that, except for the mathematical gymnastics, the unweighted exponential fit routine is the perfect solution to the data analysis. Actually, it has the same difficulties as the linear case; they are just more deeply hidden.

The unweighted least squares procedure makes use of several assumptions. It assumes that all of the errors can be associated with one variable ( $y$ ) and that errors are random (i.e., Gaussian). Goodness of fit is then determined by minimizing the sum of  $(p_i - y_i)^2$ , where  $p_i$  is the theoretical (calculated) value determined by substituting  $t_i$  into a trial

function [i.e.,  $p_i = f(t_i)$ ]. Practically a data set  $t_i, y_i$  is observed and matched to a calculated data set  $t_i, p_i$ .

Each term in the least squares sum

$$(y_i - p_i)^2 \quad (3)$$

is considered to be equally valid because each  $y_i$  is equally valid (i.e., has the same uncertainty). The problem arises from the first assumption: all the errors can be lumped into  $y$ . This implies that  $p_i$  is exact because it is calculated from  $t_i$  that is assumed to be exact. Because both  $t$  and  $y$  are experimental quantities, the validity of that assumption needs to be examined.

### 2. UNCERTAINTY ANALYSIS FOR LINEAR FUNCTIONS

For linear functions, there is no problem; and the assumption holds, viz.,

$$p_i = C t_i \quad (4)$$

If each  $t_i$  is associated with an uncertainty  $u_t$  that is constant for all  $t_i$ , then the uncertainty of  $p_i$  ( $u_p$ ) is given by

$$u_p = C u_t \quad (5)$$

and is constant for all of the calculated  $p_i$  values; and each term of the least squares sum is equally precise.

### 3. UNCERTAINTY ANALYSIS FOR NONLINEAR FUNCTIONS

For nonlinear functions, the situation is more complex. For the exponential case, equation 3 becomes

$$p_i = b \exp(-k t_i) \quad (6)$$

If the uncertainty of each  $t_i$  ( $u_t$ ) is constant, then the largest value that the calculated  $p_i$  can assume is

$$p_i \text{ (largest)} = b \exp[-k(t_i - u_t)] \quad (7)$$

$$= b \exp(-kt_i) \exp(ku_t)$$

and the smallest is

$$p_i \text{ (smallest)} = b \exp[-k(t_i + u_t)] \quad (8)$$

$$= b \exp(-kt_i) \exp(-ku_t)$$

Considering the error associated with  $p_i$  to be half the length of its error bar, then

$$2u_p = p_i \text{ (largest)} - p_i \text{ (smallest)} \quad (9)$$

$$= b \exp(-kt_i) \exp(ku_t) - b \exp(-kt_i) \exp(-ku_t)$$

$$= b \exp(-kt_i) [\exp(ku_t) - b \exp(-ku_t)]$$

Since  $b$ ,  $k$ , and  $u_t$  are constants, the bracketed factor is also a constant. Using  $A$  to represent collected constants, the net result is

$$u_p = A b \exp(-kt_i) \quad (10)$$

that, when compared to equation 6, becomes

$$u_p = A p_i \quad (11)$$

So rather than being a constant as is implicit in the normal application of the least squares analysis,  $u_p$  is a linear function of  $p_i$  or its experimental counterpart  $y_i$ .

Using relative values to relate to the chemical problem of first-order kinetics,  $y_i$  varies from 100-0%. Thus, points near 100% have twice the error as points near 50% and 10 times the error as points near 10%. Because the validity (i.e., appropriate weight) of a point relates to the inverse square of its uncertainty and because chemical reactions are typically followed for five half-lives (i.e., from 100-3%), this represents a serious problem for any type of unweighted analysis.

#### 4. CONCLUSION

The problem relates to the change in slope ( $dy/dt$ ) from a high initial value to zero at the completion of the reaction. During the first stages of the reaction, the concentration of the reactant,  $y$ , changes very rapidly. Any uncertainty of the time of a data point  $t$  in that region does not add any uncertainty to the  $y$  value of the point, but it does have a large effect on the corresponding  $p$  value because it is calculated directly from the time  $t$ . At later stages of the reaction where  $y$  is changing less rapidly, uncertainties in the time values add much less uncertainty to the calculated value of  $p$ . The net result is that the uncertainty of the  $t,y$  point is not constant for the duration of the reaction. No data analysis can be considered completely appropriate unless this is taken into account.

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